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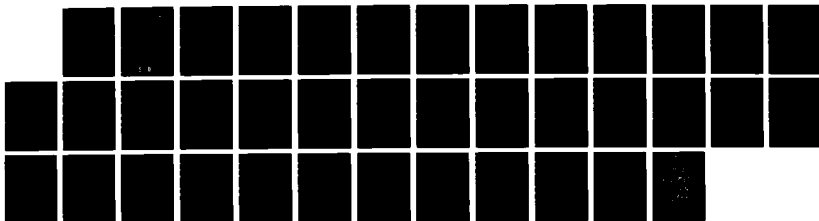
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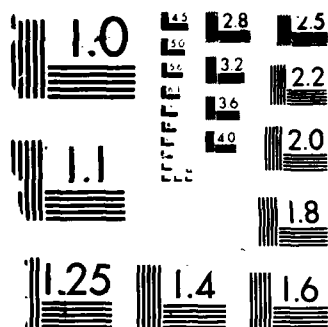
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HIGH TEMPERATURE SOLAR ELECTROTHERMAL PROCESSING-III.
ZINC FROM ZINC OXIDE AT 1200-1675K USING A NON-CONSUMABLE ANODE

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Abstract- The electrolytic decomposition potential of ZnO has been studied in a solar furnace in the temperature range 1200-1675K. The electrolyte consisted of various mixtures of CaF_2 and Na_3AlF_6 . The measured potentials were close to the thermodynamically predicted values for the reaction $\text{ZnO(s)} \rightarrow \text{Zn(g)} + 0.5\text{O}_2\text{(g)}$. The zero current overvoltages, surprisingly, increased with increasing temperature and the concurrent change in composition. The specific conductances of the electrolytes were estimated in the temperature range 1200-1500K. They increased with increasing temperature and the concurrent change in composition. Various materials were tested for use as electrodes and crucibles. Some of our experiences and our experimental techniques are described.

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INTRODUCTION

The production of a metal and oxygen from its oxide requires a net energy input of at least ΔH_f of the oxide. At least ΔG_f of that energy must be supplied as work. The remainder may be process heat. Typically, ΔG_f for metallic oxides decreases with increasing temperature; ΔH_f changes little.¹ Operating an electrolysis cell at an elevated temperature is thus a means for substituting high temperature process heat, such as that which is available from sunlight, for electrical work.

Many battery and fuel-cell systems use zinc.² It is an important commodity. The system has been studied^{3,4} and is thermodynamically well characterized. It is thus of practical as well as theoretical interest. Accordingly, we began a study of the electrolysis of metallic oxides in a solar furnace⁵ using ZnO as our prototype. In this paper we describe an extension for temperature range, 1200-1700K, where graphite casings and electrodes can no longer be used. Our objectives were to find suitable electrolytes and materials for constructing electrodes and cell casings, to design and build suitable electrolytic cells, acquire operating experience in a solar furnace with them, and measure decomposition potentials.

We measured, at approximately 100K temperature intervals, the variations of the electrical currents with the applied voltages. At the same time, we measured the potential differences between each of the cell electrodes and one of a pair of ancillary Mo electrodes (we are reluctant to call them reference



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electrodes) immersed in the electrolyte between them. These data were used to estimate the oxide zero-current decomposition potential, cell overpotential, current densities, and specific conductance of the electrolyte. The results of the study and some experiences that may be helpful to others contemplating related studies are described in this paper.

APPARATUS AND PROCEDURE

The solar furnace, instrumentation and the arrangement of receivers in it have been described previously.⁵⁻⁹ Figure 1 shows the reactor and cell assembly that were used in the present work. The cavity which housed the cell was insulated with a Cotronics 0.635 cm thick, 20 cm diameter Al_2O_3 cylinder wrapped with Carborundum Fiberfrax felt to a thickness of 5 cm. The back of the cavity was insulated with a sandwich of wrapped, 3.5 cm wide Fiberfrax felt glued with Cotronics Duralco 903 Green Ceramic Adhesive between a 2.5 cm thick Fiberfrax board and a Cotronics Al_2O_3 board, which faced the cavity. The insulation was secured with an Al plate bolted to the shell of the receiver.

The cavity was divided into two chambers by a 0.635 cm thick graphite septum perforated by six 0.635 cm holes. The cell was contained in the back chamber. During an experiment the window was swept by an Ar stream to prevent condensation of volatile materials on its surface. From there, Ar flowed through the holes in the graphite septum, into the cell. Ar left the cell through the mullite chimney tubes above the electrodes. The receiver was still working well after 100 hours of experimentation. To be on

the safe side, however, we had the window annealed after approximately every twelve hours of furnace operation to relieve thermal stresses.

The electrolytic cell is shown in Fig. 2. Its casing was made of ZrO_2 . It held four electrodes: a Mo cathode, where Zn vapor evolved; a Pt anode where O_2 formed; and two Mo ancillary electrodes. The cell sat in a graphite dish so that, if it were to crack during an experiment, the reactor cavity would be protected from the solvent.

The cell-cover was made of graphite. Holes 0.635 cm in diameter, drilled into the four corners of the cover, admitted Ar to the cell. Two 0.159 cm diameter holes held the 0.159 cm OD mullite tubes which electrically insulated the two ancillary electrodes from the cover. Two 1.91 cm diameter holes in the cover held the 1.27 cm inner diameter, 30 cm long, mullite tubes which served as chimneys for O_2 and Zn vapor. The Zn vapor was swept to a Pyrex condenser and filter. The 1.27 cm mullite tubes also supported the electrodes.

The cathode lead was Alpha Products 1.0 mm diameter Mo wire. The wire was spot welded to a 0.25 mm thick 2.54 X 1.27 cm piece of Mo foil. The wire ran from the bottom to the top of the mullite tube, where it was bent from the inside face of the tube around the top and to the outside face. The top lip of the tube thus supported the electrode. The anode was supported in a similar manner, but it was made of Alpha products 0.25 mm diameter Pt wire and 0.127 mm thick Pt foil.

We used a 0.25 mm thick Mo separator plate which extended to the crucible walls, cover, and top of the solvent, to divide the cell into separate anode and cathode compartments in an attempt to minimize recombination of the O_2 and Zn. Our electrolytes were CaF_2 - Na_3AlF_6 mixtures. Figure 3 shows that mixtures of these substances can be used to provide a wide range of melting points and volatilities in the temperature range of interest.¹⁰

Our final cell design evolved during the course of our experimental work. We worked with a variety of materials and structures, some of which were not successful,¹¹ observing the maxim that good judgement comes with experience and that bad judgement often provides the mechanism by which one gains experience. To provide others who may wish to do related experiments with the benefit of our experiences, we have provided an abstracted description of the evolution of the cell in the Results and Discussion section.

We used a Doric Digitrend 235 data logger and an IBM personal computer for retrieving and manipulating experimental data. Data were stored on a floppy disk. Figure 4 shows the electrical measurements system. Direct current was supplied to the electrodes on a circuit that was separate from the circuits used to measure the voltages. The cell-voltage measuring circuit included a high impedance voltmeter. The reported cell-voltages, therefore, do not include any significant IR drop in the leads to the electrodes. We measured the total potential difference across the cell and the potential of each electrode with respect to one of a

pair of ancillary-electrodes (Mo wires, 1 mm diameter) electrically insulated in mullite tubes. They were in the nature of reference electrodes, but inasmuch as at this point in our research we had neither well characterized reference electrodes nor a data base of standard electrode potentials for comparison, our purposes were better served by the present arrangement than they would have been by a more conventional one. The anode, cathode, and the two ancillary-electrodes were arranged in a straight line, as is shown in Fig. 4; they were spaced, nominally, 2.54 cm apart. We measured current with the ammeter depicted in Fig. 4 as the shunted voltmeter.

With the back-plug of the receiver removed, the cell was first loaded with electrolyte. Then, J.T. Baker reagent grade zinc oxide was added to make a 5% mixture. We wished to work with saturated solutions so that the activity of ZnO in the electrolyte would be that of solid ZnO. The solubility of ZnO in Na_3AlF_6 at 1300K is 0.53%⁵ by weight. We assumed that our solutions would be saturated at all the temperatures of the present study.

One thermocouple was placed on the cell to measure its temperature; another was placed near the back of the cavity. The anode and cathode, shrouded and supported by mullite tubes, were then inserted through the top of the receiver, to just above the electrolyte surface. The mullite tubes were supported by clamps which rested on the receiver shell. The insulating plug was then inserted, and the back plate of the reactor bolted on. The electrical connections were then made, the condenser and the filter were installed, the window was secured to the front of the re-

ceiver, and the flow of Ar, about 5 l/min, begun.

The heliostat was set to track with the doors closed. The instrumentation was activated. Then both furnace doors were fully opened to start heating up the reactor. As the cell temperature approached the test temperature, we diminished the power to the reactor by partially closing the furnace doors. Once the temperature reached the desired operating temperature and became steady, we began the electrolysis by increasing voltage across the cell in approximately 0.25 volt increments.

Data were recorded every 7 seconds. We took at least 3 data points at each voltage setting. The voltage was increased to about 3 volts and then reduced to 0 volts. We increased and decreased the voltage in this manner at least two times. Then we set the voltage to a specific value and electrolyzed over a given period of time at that voltage.

At the end of an experiment, we closed both doors, stowed the heliostat and reopened the doors to provide good ventilation to the concentrator room. Then we disconnected the condenser and filter, removed the electrodes, and let the receiver cool. When its temperature reached 500K we turned off the flow of Ar.

RESULTS AND DISCUSSION

Decomposition Potentials

We plotted the current versus applied voltage to determine the decomposition potentials of ZnO at the cell's operating

condition. Figure 5 is an idealized example of such a plot. Such a curve contains two regions. A region of very low conductivity (slope) followed, at higher voltages, by a region where the conductivity is higher and the current is a linear function of the applied voltage. The low-conductivity region may indicate a condition in which the products interact with the electrodes in such a way as to reduce their activity, or it may simply indicate the presence of an impurity in very low concentration. We assume that the straight line region indicates the condition where Zn and O_2 are being produced at 1 atm. Accordingly, we represented the variation of the the decomposition potential with voltage by fitting, by least squares, a straight line to all data points with voltages greater than the theoretical zero current potential of the cell. The point at which this line crosses the abscissa is thus the zero-current decomposition potential of ZnO measured in this cell.

Figure 6 is an example of a typical plot of the variation of current with voltage. The operating temperature was 1500 K. The electrolyte was $0.85CaF_2-0.15Na_3AlF_6$. We used a ZrO_2 crucible, a Pt anode, and a Mo cathode. The zero current potential in this experiment was 1.0 volt, which is to be compared to the theoretical standard potential for the formation of Zn and O_2 , each at 1 atm, 0.85 volt. The difference, 0.15 volt, is the overpotential.

All our plots in the range 1200-1500 K were similar. However, a portion of the mullite tube broke and fell into the solvent during the 1600K experiment. Thus, small amounts of Al_2O_3 and SiO_2 were contained in the electrolyte of the 1600 and 1675K

experiments. These experiments produced voltage-current curves like that shown in Fig. 7.

Figure 7 presents the results of the 1600K experiment. The solvent was $0.9\text{CaF}_2-0.1\text{Na}_3\text{AlF}_6$. The curve suggests that two different concurrent electrolytic processes occurred; the graph shows two straight-line regions, which we attributed to the electrolysis of ZnO and Al_2O_3 . We determined the experimental zero-current decomposition potential of ZnO , 0.86 volt, by fitting a straight line to data points with voltages greater than 0.74 volt, the theoretical decomposition potential of ZnO , but less than 2 volts. A least-squares fit of the data-points above 2 volts gave, at the point where the two lines intersect, an experimental zero-point decomposition potential for Al_2O_3 of 2.09 volts, which is to be compared with the theoretical value, 2.03 volts. Our interpretation of the result was supported by an auger microspectroscopic analysis of the cathode product, which found both Zn and Al.

Figure 8 presents the variation of the zero-current decomposition potentials of ZnO with temperature over a range 1200-1675K. It also gives the compositions of the electrolytes. The composition we used at a particular temperature was that which would just become completely molten at that temperature. All data points except that of solvent F were determined using a ZrO_2 crucible, a Pt anode, and a Mo cathode. In the solvent F experiment we used a graphite crucible, a Pt anode, and a Mo cathode. The line is the theoretical standard state decomposition poten-

tial.

Overvoltages

Table 1 shows the zero-current overvoltages. Two values are given for each experimental condition. Because we measured our voltages at a point where the temperature was less than that of the electrolyte, a Pt-Mo thermocouple may exist in the voltage measuring circuit (Fig. 4). Our experimental overvoltage might thus be in error by the amount of the thermocouple effect. Two overvoltages are therefore reported at each temperature in Table 1. The lower value has been corrected for the thermocouple effect. The upper value is uncorrected. The low value reported in the table is the result we get when we subtract out the thermocouple effect.¹² The high value is the result we obtain when we neglect the effect.

The zero current overvoltage increased with increasing temperature from 1200 to 1500 K; then it decreased. One might expect these overvoltages to decrease monotonically with increasing temperature, because they usually stem from activation energy controlled reaction rates.

Conductance of the Electrolytes and the Cell

We estimated the specific conductances of the electrolytes as follows. We measured the potential differences between the two Mo ancillary electrodes and the cell currents. The conductances of the electrolytes between the two Mo ancillary electrodes and their separation was thus known. To calculate specific conduct-

ances, one must know the cross-sectional-area of the conduction path, effectively, a cell constant, and have information about how the active electrode area is related to its geometric area. Lacking such information, we simply used the area of our electrodes.

Table 2 shows the results. Although we could find no data in the literature on the specific conductances of these electrolytes, we were pleased to note that the specific conductances, albeit they were rudely measured, and their dependences on temperature were comparable to those of the electrolytes used in the Hall-Heroult process.¹³

We have also listed the cell conductances obtained from the slope of the straight line portion of the current-voltage curves in Table 2. Both the specific conductance of the electrolyte and the conductance of the cell increased with increasing temperature, suggesting that the power required to produce Zn at a given rate will decrease as the temperature increases and concurrent changes are made in the solvent's composition.

Current Densities

Figure 9 shows how the current density varied with the voltage, and the (coupled) temperature and solvent composition. We calculated the current density by dividing the current by the superficial electrode surface area. The current density, a measure of the Zn production rate, increased at all voltages as the temperature increased and the solvent composition changed.

An Approach to Measuring Single-Electrode-Potentials

The primary measurements of this study were of the characteristics of the electrolysis cells and the behavior of their components themselves in a solar furnace. Nevertheless, it would be desirable if there were a set of single-electrode-potentials analogous to those which are the basis for more conventional electrochemical studies. Accordingly, we measured the potential differences, with very little current flow through their circuits, of each of the cell's electrodes with respect to its own Mo ancillary electrode using the set-up shown in Fig. 2.

Figure 10 is a plot of the variation, with the current through the cell, of the voltage of the anode with respect to its molybdenum ancillary electrode. In this experiment, which was done in a ZrO_2 crucible, the electrolyte was cryolite. The anode was Pt and the cathode was Mo. Extrapolation of the line to zero current gives an emf of +1.06 volt for the anode with respect to its Mo ancillary electrode with no current flowing through the cell.

Figure 11 is a plot of the variation, with the current through the cell, of the absolute value of the (negative) voltage of the cathode with respect to its Mo ancillary electrode in the same experiment. Extrapolation of the line to zero current gives an emf of -0.05 volt for the Mo cathode with respect to its Mo ancillary electrode with no current flowing through the cell.

Table 3 presents the results of the experiments done in the range 1200-1500K. The 1600 and 1675K experiments gave ambiguous

results, perhaps because of the presence of the mullite fragment we referred to earlier.

Current Efficiencies

Current efficiencies for the production of Zn, the Zn yields divided by the theoretical yields based on Faraday's law, are reported in Table 4. Table 4 also describes the pertinent features of the experiment having to do with the current yield. Current efficiencies ranged from 0.39 to 0.89. It is noteworthy that the current efficiency seemed to depend on our ability to keep the cathode and anode section of the cell separated so that the products cannot mix. It is thus a measure of our ability to design and build good electrolytic cells. This should improve with experience.

Steady Operation

In some of our experiments electrolysis occurred at a set current level for approximately 30 minutes. In every instance the current was stable; the cell resistance remained constant over the time of the run. Figure 12 shows a typical observation. It is a plot of the variation of current and cell resistance with time during the electrolysis of ZnO in a ZrO_2 crucible with a Pt anode and a Mo cathode. The operating temperature was 1400 K. The electrolyte was $0.75 \text{ CaF}_2 - 0.25 \text{ Na}_3\text{AlF}_6$. The current stability, as shown in Fig. 12, suggests that the ions that are participating in the electrode reactions are being replenished at a rate fast enough to maintain a stable current level and that the electrodes

do not seem to be changing as a result of the electrolytic process.

SOME GENERAL OBSERVATIONS

Much of what we learned about the conduct of electrochemical experiments in solar furnaces does not lend itself to a precise systematic description, nor did we conduct systematic studies of material properties or the behavior of cell components. Nevertheless, what we learned may be helpful to other investigators. We are therefore presenting some of our observations in narrative form here.

Electrodes

In our previous work we found that in the temperature range 1200-1400K ZnO reacted spontaneously with a graphite cathode, as is to be expected from the thermodynamics of this system, to produce CO and Zn. This reaction produced an insulating gas film around the cathode. The result was that the decomposition potential apparently increased with increasing temperature.⁵ We therefore, elected to replace the graphite cathode with a metallic one.

We first attempted to electrolyze ZnO in Na_3AlF_6 at 1300K using Pt electrodes. The process worked well for thirty minutes. We were able to estimate a decomposition potential, but the cathode, which was 220K above the boiling point of Zn, eventually alloyed with the Pt, causing it to melt. We then tried the experiment at higher temperatures to see if raising the temperature

might eventually make the cathode invulnerable to attack because of the increased volatility of the Zn. At 1400K, 320K above the boiling point of Zn, the cathode again failed, however. We then abandoned attempts to use Pt for cathodes and considered the use of Mo, W, and Ta.

These elements have been reported as not forming alloys with Zn.¹⁴ We put foils of each of these metals in contact with ZnO at 1400K for fifty minutes. Their fractional weight changes were +0.00102 for Mo, +0.024 for W, and -0.081 for Ta. Moreover, ZnO had a tendency to stick to the W and the Ta but not to the Mo. All of the metals changed color; Mo turned black, W turned white, and Ta became gray. We chose Mo because it underwent the smallest weight change.

Mo cathodes lasted for as long as 12 hours in our cells at temperatures ranging from 1200-1675K. It became brittle and sometimes broke as we handled it between experiments. With proper handling, though, Mo is a suitable material for a cathode in a laboratory solar electrolytic process that produces Zn from ZnO.

Platinum is a good anode material. The only times we lost Pt electrodes were when they came in contact with Zn vapor. Because of the high cost of Pt, we sought techniques to reduce the cost of Pt electrodes. We painted Pt black onto a zirconia tube, and placed the tube into a zirconia crucible containing $0.25\text{CaF}_2 - 0.75\text{Na}_3\text{AlF}_6$. Then we brought the crucible up to 1200K in the solar furnace, and held that temperature for fifty minutes. The tube was not damaged, and the Pt paint remained conductive. We

therefore believe that that Pt painted zirconia tubes may have some potential as working electrodes in a ZnO reduction process. It has been suggested, and is attractive to consider, that ZrO_{2p} cells with only the gas-side painted with Pt might be used, thus obviating the need to have Pt in contact with the electrolyte at all, but we did not try such a procedure.

Electrolytes

The electrolyte was various mixtures of Alpha 98.5% Na_3AlF_6 and J.T. Baker 99% CaF_2 . The use of mixtures of varying composition permitted us to run all of the experiments just above the melting points of the mixtures.¹⁰ We were thus able to minimize the volatility of the electrolyte, avoiding its loss and fouling of the window.

Cell Casings

In our previous study,⁵ we used a graphite cell casing. At temperatures above 1100K, the oxide was reduced by the graphite, making it impossible for us to determine current yields. We therefore had to develop a cell casing that would not reduce the oxide at our operating temperatures.

Molybdenum was our first candidate material. Eventually, the design which evolved worked well.¹¹ It was constructed of 0.25 mm thick Alpha products Mo foil. The foil was folded into the shape of a rectangular basket with tapered walls. The tapered walls permitted us to remove the solvent from the cell casing easily at the end of an experiment. To help protect the reactor in the

event of a leak, we placed the basket into a graphite dish. Molybdenum is said to become brittle in contact with graphite at high temperatures.¹⁵ We therefore separated the cell casing and the graphite with ZrO_2 felt. After eight hours of experimentation with this cell casing, it is still usable.

Unfortunately, Mo cell casings are also good electrical conductors. During experiments in which we placed a Mo sheet plate across the cell casing to separate the anode and cathode products the Pt anode was destroyed. Apparently, a short circuit permitted the reduction of Zn^{+2} directly below the anode, and the Zn which formed destroyed it. We had the choice of changing the cell casing's geometry to move the electrodes closer together and deepen the cell casing, or to make a less conductive cell casing. We chose the latter alternative.

We decided to work with ZrO_2 . We cast a cell casing from Owen Corning Zircoa Cast 28D with their Zircoa Bond 6. This cell casing showed no signs of damage under any of our operating conditions, and it was used for eight hours of experimental work.

Acknowledgements- We thank the Office of Naval Research and The Northern States Power Company for their generous support of this research. Todd Kappauf and Donald Parks contributed substantially to the research through many discussions as well as in the conduct of experiments.

REFERENCES

1. E.A.Fletcher and J.E. Noring, Energy 8, 247 (1983).
2. C.H. Mathewson, Zinc: The Metal. Its Alloys and Compounds. Reinhold Publishing Corp., New York, NY (1959)
3. D.P. Zosimvich and V.A. Tsimergaki, Ukrain. Khim. Zhur. 15, 351 (1949).
4. V.N. Andreeva, Ukrain. Khim. Zhur. 21 (1955).
5. E.A.Fletcher, F. Macdonald, and D. Kunnerth, Energy 10, 1255 (1985).
6. R.B.Diver, D.E.E.Carlson, F.J.Macdonald, and E.A.Fletcher, J. Solar Energy Engineering 105, 288 (1983).
7. D.E.E.Carlson, R.B.Diver, and E.A.Fletcher, J. Solar Energy Engineering 106, 106 (1983).
8. R.B.Diver, S.Pederson, T.Kappauf, and E.A. Fletcher, Energy 8, 947 (1983).
9. T.Kappauf, J.P.Murray, R.Palumbo, R.B.Diver and E.A.Fletcher, Energy 10, 1119 (1985).
10. E.M.Levin and H.F.McMurdie, "Phase Diagrams for Ceramists 1975 Supplement," p.368 Compiled at the National Bureau of Standards, edited and published by the American Ceramic Society, Inc., New York, NY (1975).
11. R.D.Palumbo, Ph.D. Thesis, University of Minnesota, Minne-

apolis, MN. 55455 (1987).

12. Wm.F.Roeser and H.T.Wensel, "Appendix to the book Temperature. Its Measurement and Control in Science and Industry, p.1310, papers presented at a symposium held in New York City in November 1939 under the auspices of the American Institute of Physics with Cooperation of the National Bureau of Standards and the National Research Council, Reinhold Publishing Co.,

13. Encyclopedia of Chemical Technology, 3rd ed., Vol 2, John Wiley and Sons, New York, NY (1978).

14. M. Hansen, Constitution of Binary Alloys, 2nd ed., McGraw Hill, New York, NY (1958).

15. S. Hopkins, Chapters in the Chemistry of Less Familiar Elements, Stipes Publishing, New York, NY (1937).

Table 1. Zero current overpotentials.

| T, K | Mole fraction CaF ₂ in electrolyte | Overvoltage, volts ^a |
|------|---|------------------------------------|
| 1200 | 0.50 | -0.01 and 0.01 |
| 1300 | 0.25 | 0.07 and 0.09 |
| 1300 | 0.0 | 0.02 and 0.05 |
| 1400 | 0.75 | 0.09 and 0.12 |
| 1500 | 0.85 | 0.12 and 0.15 |
| 1600 | 0.90 | 0.08 and 0.12 |
| 1675 | 0.90 | 0.0 and 0.04 |

^aAs we noted in the text, the Pt-Mo electrodes may form a thermocouple and develop a voltage. Such a voltage would be measured in this experiment, but it would not really be a component of the potential across the cell. The lower value reported for the overvoltage includes a correction for the thermocouple effect. The higher value is the uncorrected value.

Table 2. Cell and specific conductances.

| Mixture ^a | T.K | Cell Conductance ohm | Sp. Conductivity ohm ⁻¹ cm |
|---|------|-------------------------|--|
| 0.45CaF ₂ 0.45Na ₃ AlF ₆ 0.10ZnO | 1200 | 1.8 | 6 |
| 0.88Na ₃ AlF ₆ 0.12ZnO | 1300 | 2.0 | 8 |
| 0.69CaF ₂ 0.23Na ₃ AlF ₆ 0.08ZnO | 1400 | 2.5 | 9 |
| 0.79CaF ₂ 0.13Na ₃ AlF ₆ 0.07ZnO | 1500 | 3.0 | 15 |
| ^a We are not aware of any solubility data for these systems, but it is quite likely that there is more-than-enough ZnO in these mixtures to saturate the liquid phase. | | | |

Table 3. Electrode potentials with respect to their Mo ancillary electrodes.

| T, K | Mole fraction CaF_2 in electrolyte | Cathode, volts | Anode, volts |
|------|---|----------------|--------------|
| 1200 | 0.50 | -0.11 | +1.0 |
| 1300 | 0.25 | -0.05 | +1.09 |
| 1300 | 0.0 | -0.05 | +1.06 |
| 1400 | 0.75 | -0.02 | +1.05 |
| 1500 | 0.85 | 0.0 | +0.95 |

Table 4. Current efficiencies.

| T,K | Experimental condition | Current efficiency |
|---|--|--------------------|
| 1200 | Zirconia crucible with 0.50 loose Mo partition separating cathode and anode compartments | 0.50 |
| 1300 | Zirconia crucible with 0.50 loose Mo partition separating cathode and anode compartments | 0.55 |
| 1400 | Mo crucible without a 0.39 partition between the cathode and the anode compartments | 0.39 |
| 1400 | Zirconia crucible with 0.72 a tight Mo partition separating the cathode and anode compartments | 0.72 |
| 1500 | Zirconia crucible with 0.72 a tight Mo partition separating the cathode and anode compartments | 0.66 |
| 1600 ^a | Zirconia crucible with 0.72 a tight Mo partition separating the cathode and anode compartments | 0.89 |
| 1675 ^a | Zirconia crucible with 0.72 a tight Mo partition separating the cathode and anode compartments | 0.89 |
| ^a Al also formed in this experiment. | | |

FIGURE CAPTIONS

Fig. 1. The cell assembly within the receiver. The left chamber is the cell cavity. It is separated from the right chamber by the perforated graphite disc. Argon flow prevents condensation of volatiles from the cell on the window and sweeps the electrolysis products from the receiver.

Fig. 2. Schematic diagram of the electrolytic cell.

Fig. 3. Phase diagram of the $\text{CaF}_2\text{-Na}_3\text{AlF}_6$ system. This diagram is taken from Ref. 10. The temperature is in $^{\circ}\text{C}$.

Fig. 4. Schematic diagram of the electrical-measurements system.

Fig. 5. Idealized example of a current-voltage plot.

Fig. 6. Typical example of the variation of current with applied voltage for the electrolysis of ZnO . Experimental details for this experiment are shown on the figure.

Fig. 7. Example of an experimental result obtained using an electrolyte which had been contaminated with mullite as a consequence of the the breakage of an electrode shroud.

Fig. 8. Variation of the experimentally measured zero-current decomposition potential of ZnO with temperature and and electrolyte composition. The line is the theoretical value.

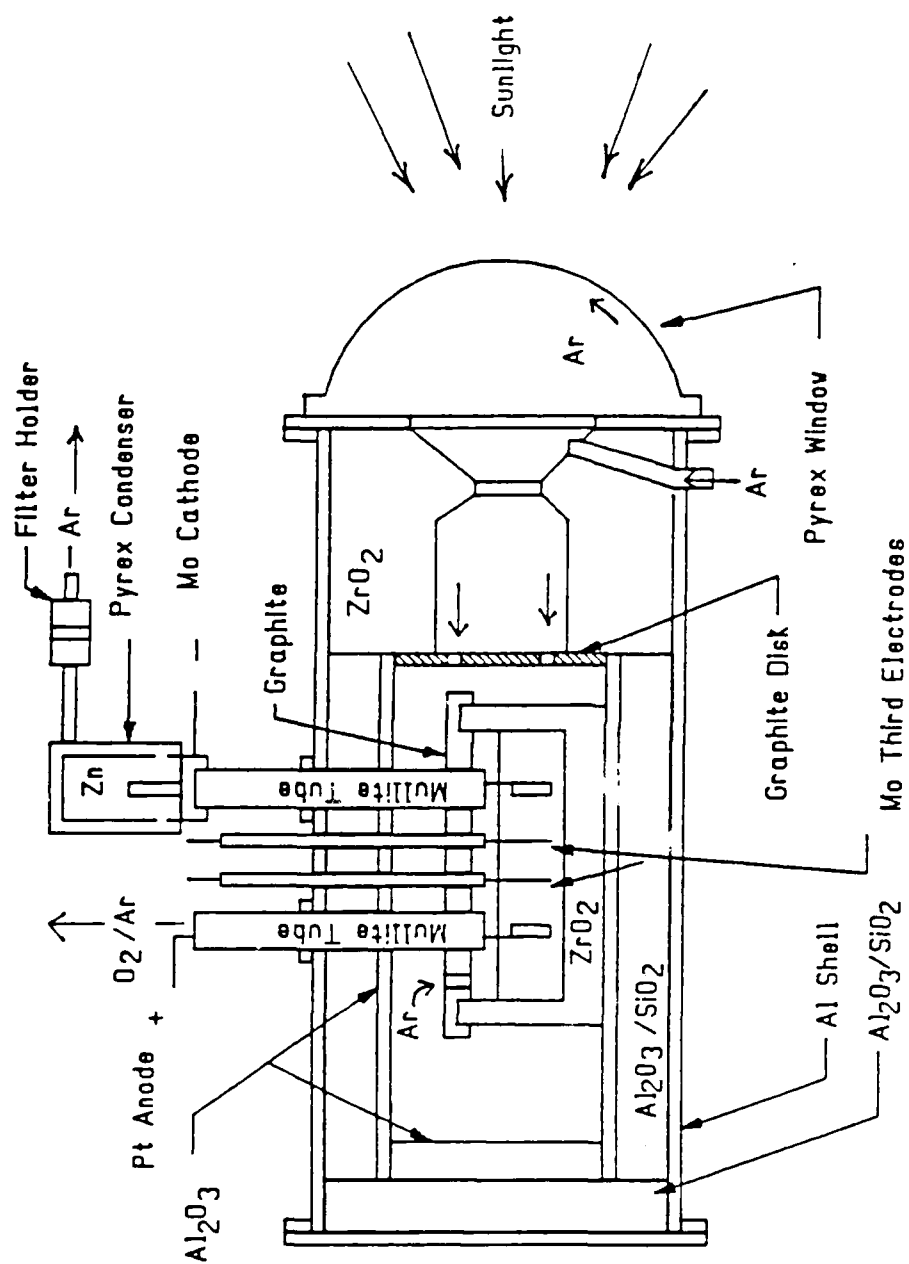
Fig. 9. Variation of the current density with temperature.

Changes in the electrolyte composition with temperature are also indicated. The applied voltage is a parameter.

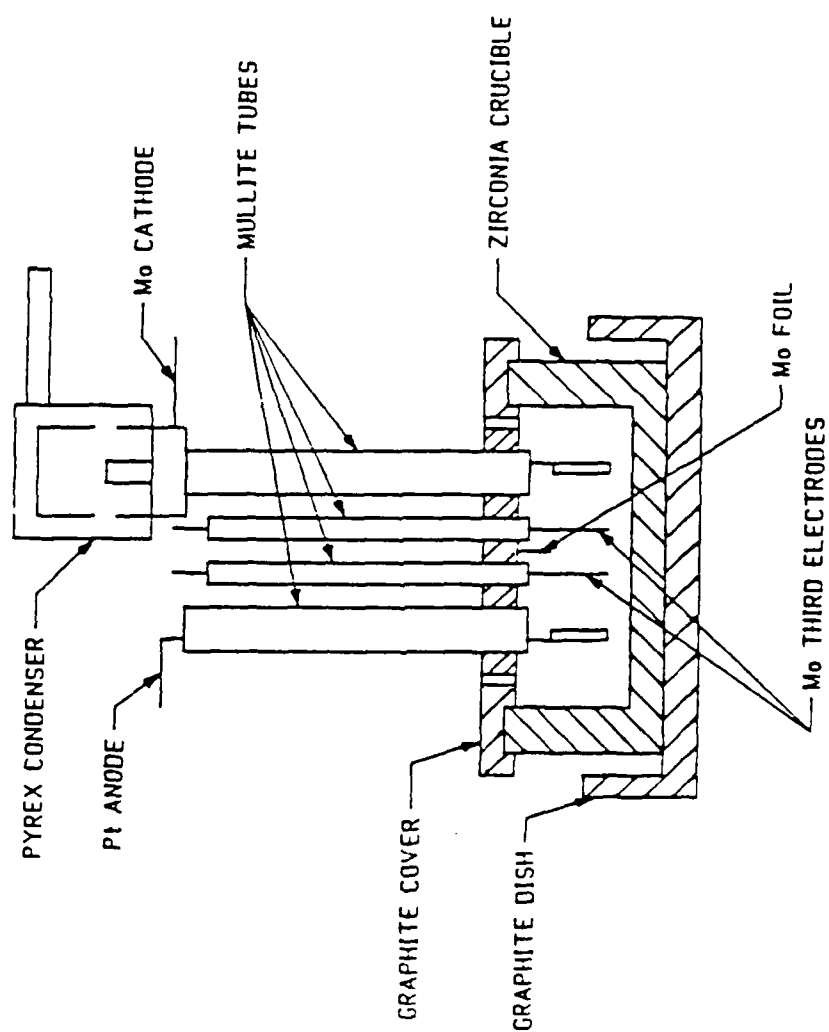
Fig. 10. Variation of the potential of the anode with respect to its ancillary Mo electrode, with the voltage applied to the cell at 1300K.

Fig. 11. Variation of the absolute value of the (negative) potential of the cathode with respect to its ancillary Mo electrode with the voltage applied to the cell at 1300K.

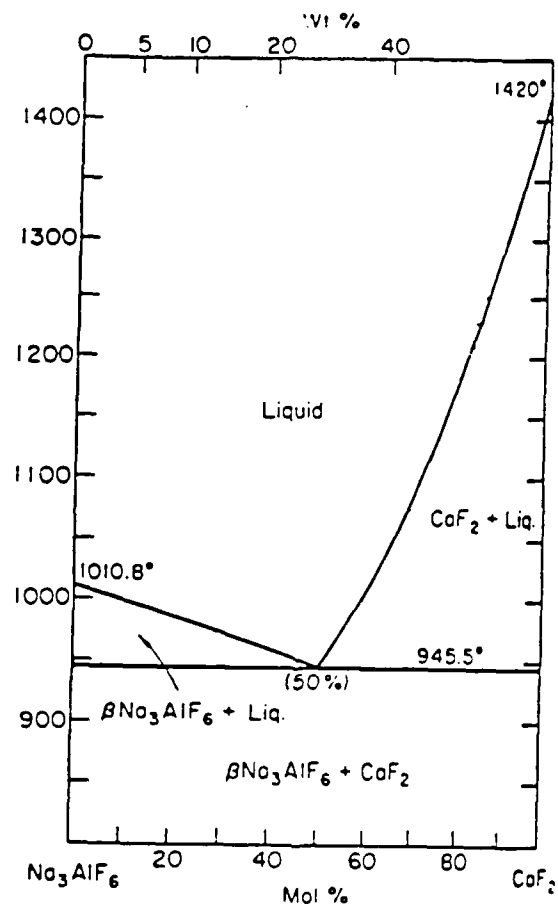
Fig. 12. Variation of the current and the cell resistance during the course of a 56 minute electrolysis of ZnO at 1400K. The electrolyte was $0.75\text{CaF}_2-0.25\text{Na}_3\text{AlF}_6$.



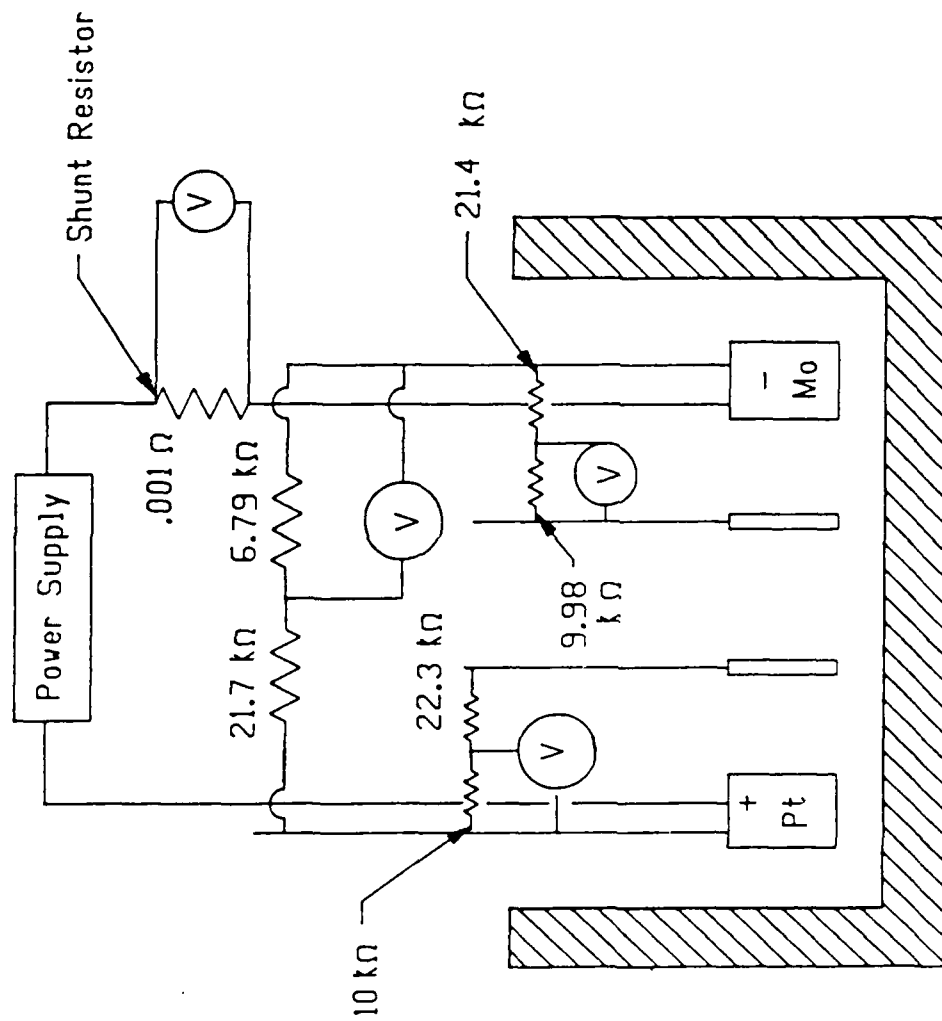
PALUMBO & FLETCHER
FIGURE 1



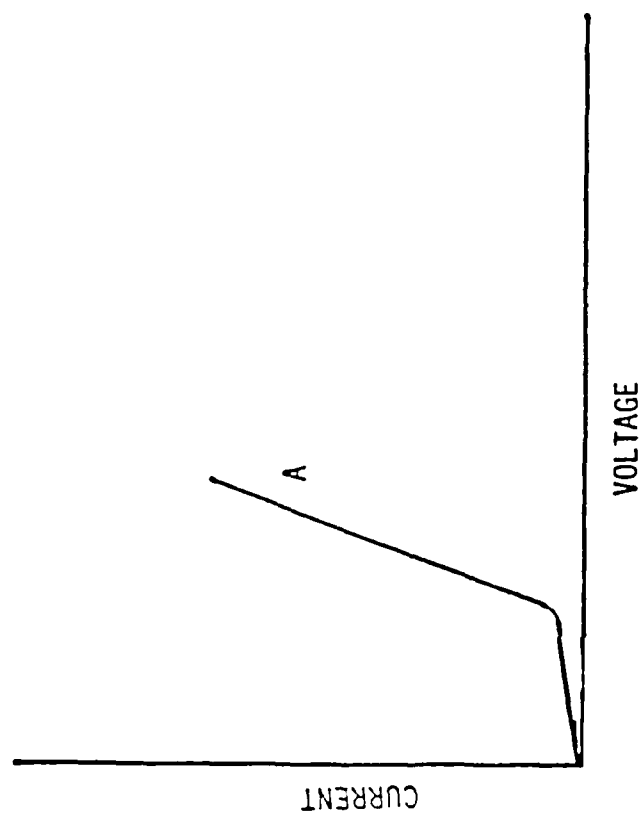
PALUMBO & FLETCHER
FIGURE 2



PALUMBO & FLETCHER
FIGURE 3



PALUMBO & FLETCHER
FIGURE 4

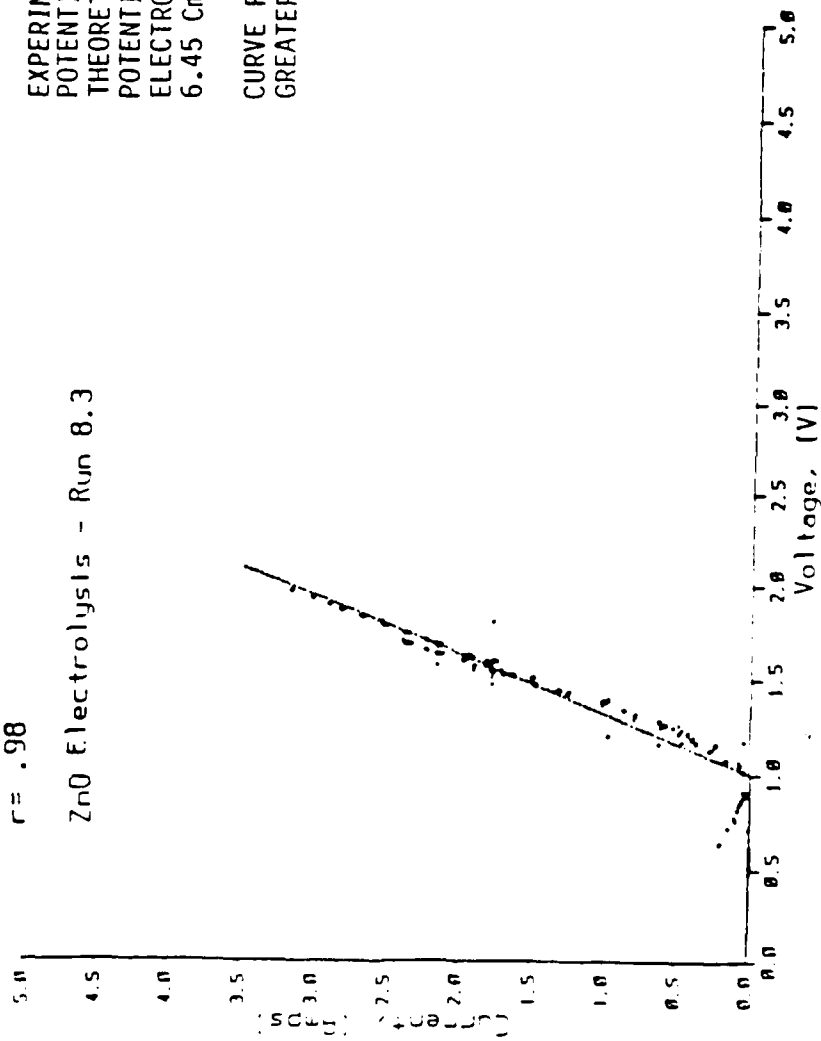


PALIMBO & FLETCHER
FIGURE 5

OPERATING TEMPERATURE: 1500 K
 ZIRCONIA CRUCIBLE; Pt-ANODE; Mo-CATHODE
 SOLVENT: 85 MOLE% CaF_2 , 15 MOLE% CRYOLITE
 DATA DISK RECORD NUMBERS 546-900

$r = .98$

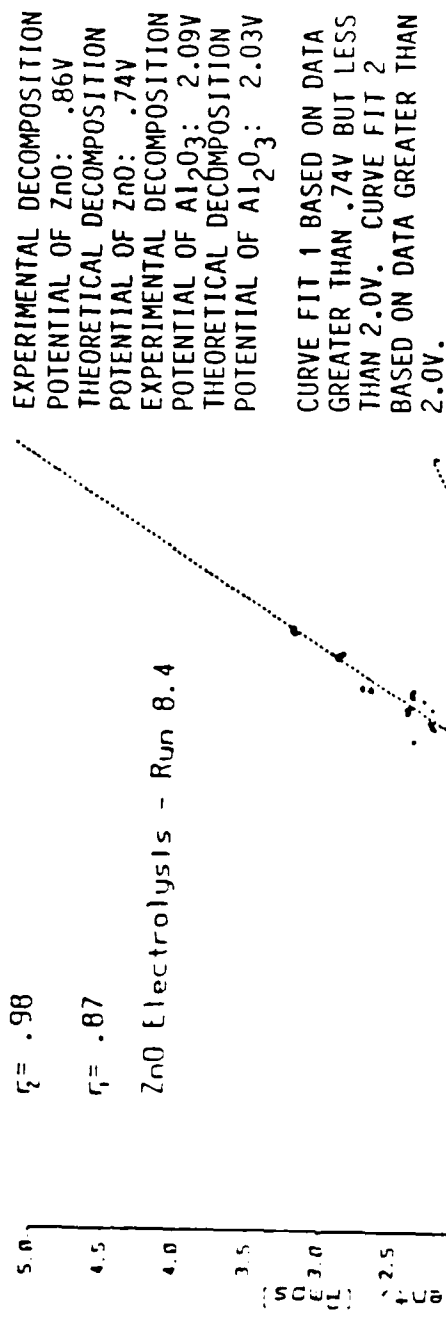
ZnO Electrolysis - Run 8.3

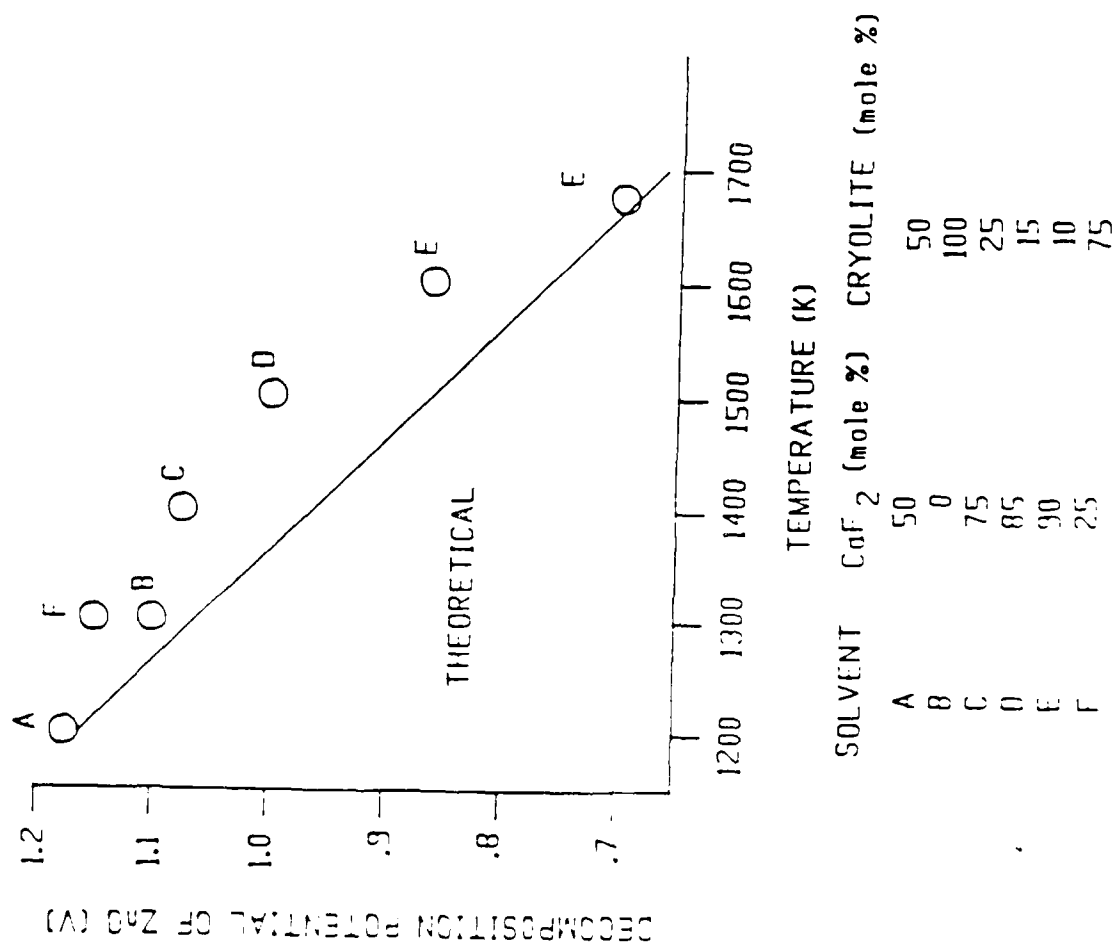


EXPERIMENTAL DECOMPOSITION
 POTENTIAL 1.0V.
 THEORETICAL DECOMPOSITION
 POTENTIAL .85V.
 ELECTRODE SURFACE AREA:
 6.45 cm^2 .

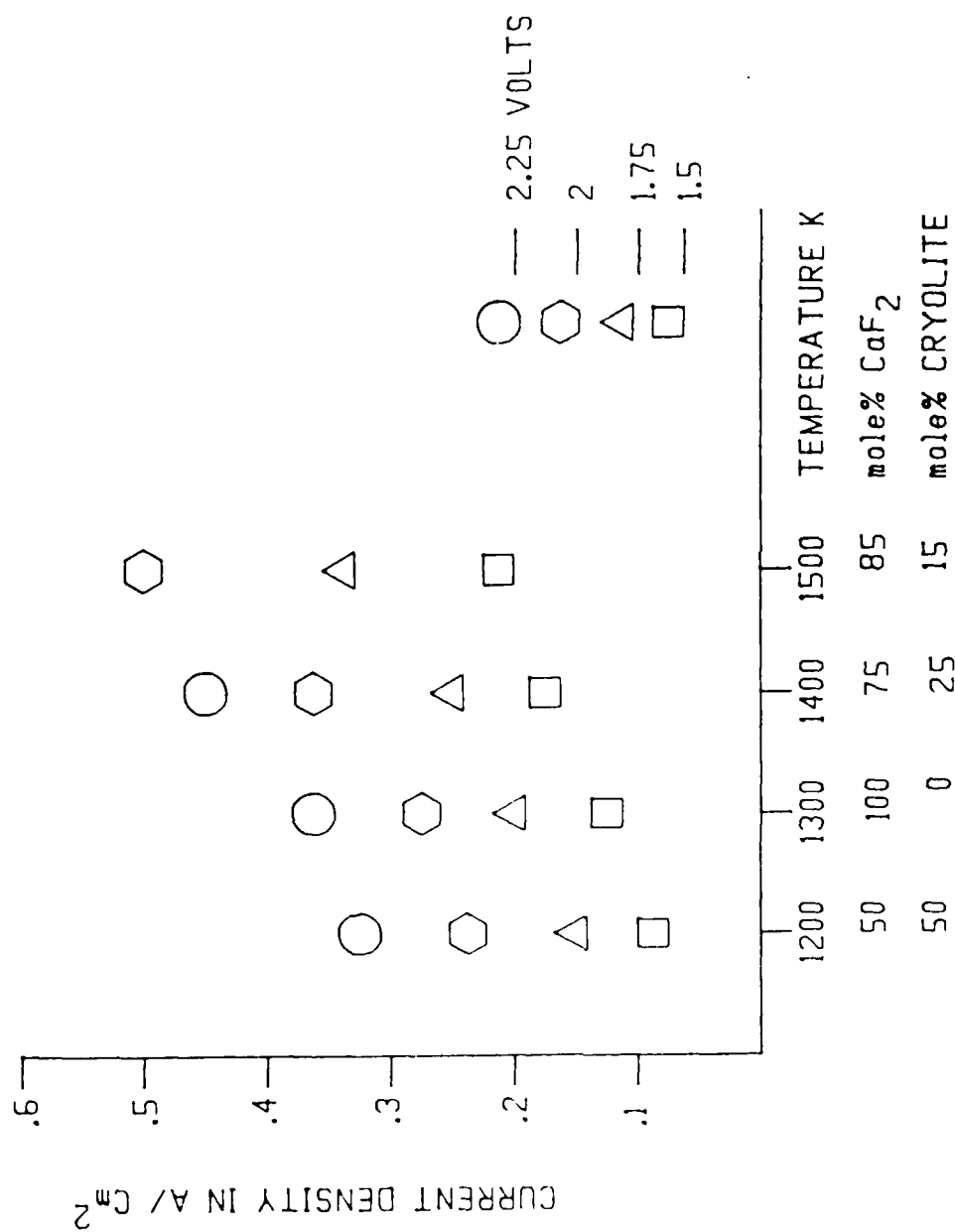
CURVE FIT BASED ON DATA
 GREATER THAN .85V.

OPERATING TEMPERATURE: 1600 K
 ZIRCONIA CRUCIBLE; Pt-ANODE; Mo-CATHODE
 SOLVENT: 90 MOLE% CaF_2 ; 10 MOLE% CRYOLITE
 DATA DISK RECORD NUMBERS 365-500

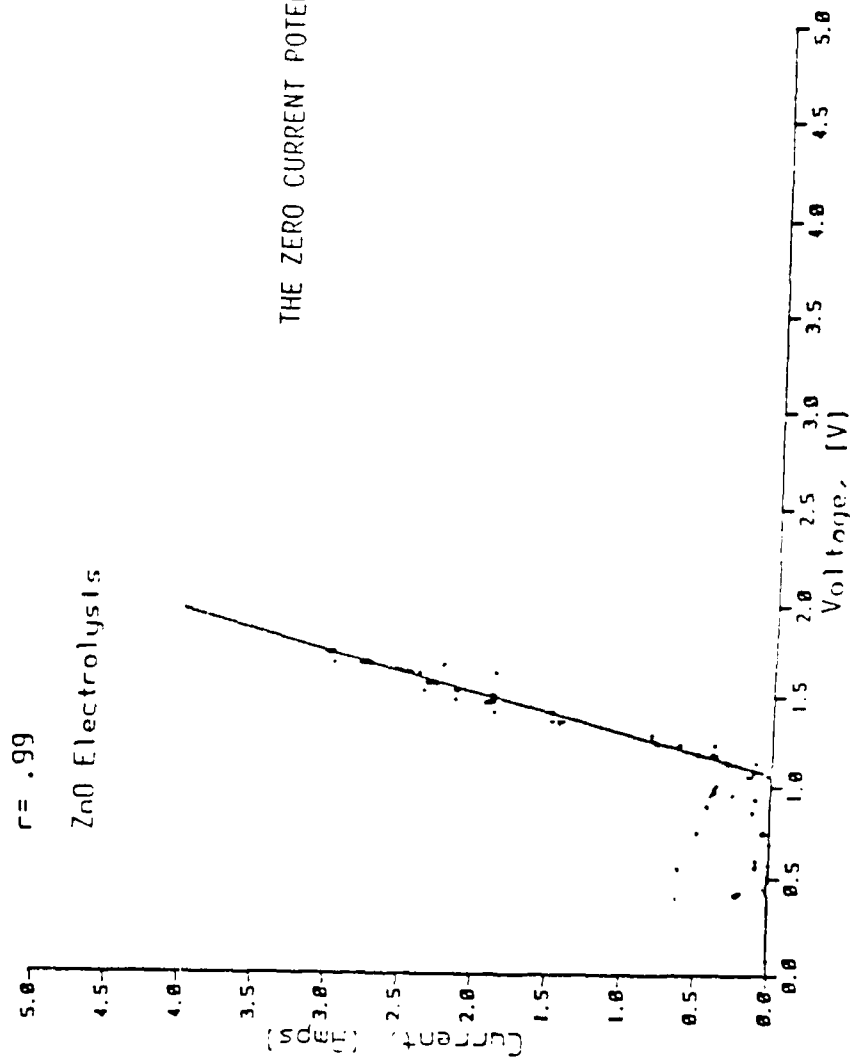




PALUMBO & FLETCHER
FIGURE 8

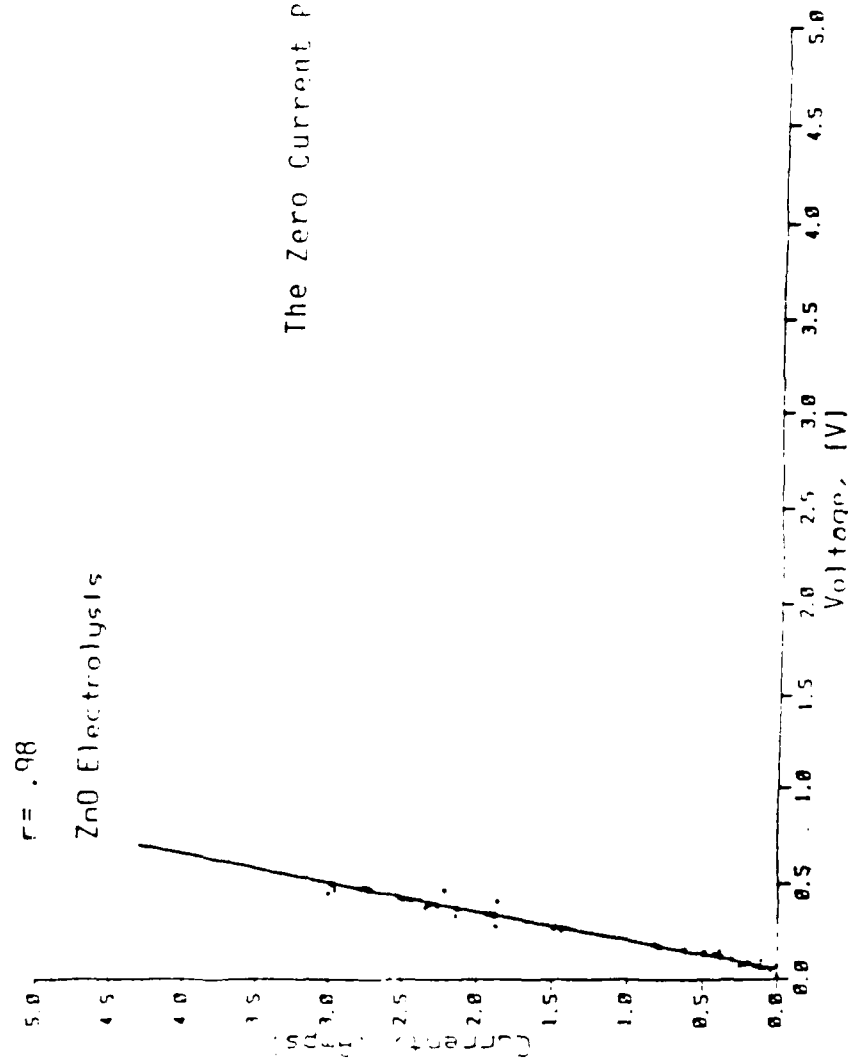


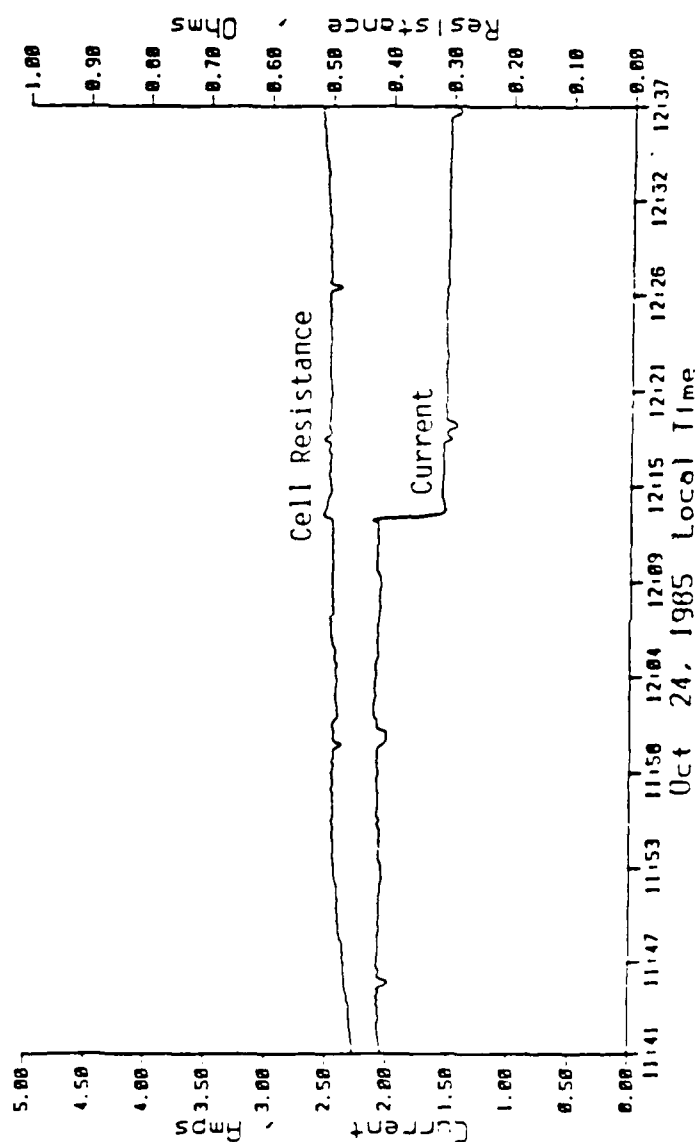
OPERATING TEMPERATURE: 1300 K
ZIRCONIA CRUCIBLE; Pt-ANODE; Mo-CATHODE
SOLVENT: 100% CRYOLITE
DATA DISK RECORD NUMBERS 813-1000



PALUMBO & FLETCHER
FIGURE 10

OPERATING TEMPERATURE: 1300 K
 ZIRCONIA CRUCIBLE; Pt-ANODE; Mo-CATHODE
 SOLVENT: 100% CRYOLITE
 DATA DISK RECORD NUMBERS 813-1000





PALUMBO & FLETCHER
FIGURE 12

END
DATE
FILMED
JAN
1988